Reactions of 3-Chloro-2-(trimethylsiloxy)prop-1-ene with Low-valent Metal Complexes. Syntheses of Metallacyclobutan-3-ones of Osmium, Iridium, and Platinum and the *X*-Ray Structure of Chloro(carbonyl)bis(triphenylphosphine)iridacyclobutan-3-one

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The low-valent metal complexes, $[\text{IrH(CO)(PPh}_3)_3]$, $[\text{Pd(PPh}_3)_4]$, and [Pt(*trans*-stilbene)$(\text{PPh}_3)_2$] catalyse the isomerisation of the ketone $\text{Me}_3\text{SiCH}_2\text{C(O)CH}_2\text{Cl}$ to the silylenol ether $\text{CH}_2\text{=C(OSiMe}_3)\text{CH}_2\text{Cl}$ which reacts with $[\text{Os(CO)}_2(\text{PPh}_3)_3]$, $[\text{IrH(CO)(PPh}_3)_3]$, $[\text{IrH(CO)}_2(\text{PPh}_3)_2]$, *trans*-$[\text{IrCl(CO)(PPh}_3)_2]$, and [Pt(*trans*-stilbene)$(\text{PPh}_3)_2$] to afford the metallacyclobutan-3-ones $[\overline{\text{Os}\{\text{CH}_2\text{C(O)C}}\text{H}_2\}(\text{CO})_2(\text{PPh}_3)_2]$, $[\overline{\text{Ir}\{\text{CH}_2\text{C(O)C}}\text{H}_2\}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$, and $[\overline{\text{Pt}\{\text{CH}_2\text{C(O)C}}\text{H}_2\}(\text{PPh}_3)_2]$; the *X*-ray structure of the title complex (**3**) establishes the presence of a puckered iridacyclobutan-3-one ring [fold angle 41°].

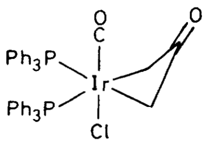
The utility of the push–pull precursor (**1**) in the synthesis of trimethylenemethane metal complexes[1,2] led us to investigate the use of other such reagents *e.g.* (**2**) in organometallic synthesis.

Treatment of the ketone (**2**) [readily available from $\text{Me}_3\text{SiCH}_2\text{MgCl}$ and $(\text{CH}_2\text{ClCO})_2\text{O}$[3]] with $[\text{IrH(CO)(PPh}_3)_3]$ in refluxing toluene for 10 min afforded the iridacyclobutan-3-one complex (**3**) in quantitative yield.† An excess of (**2**) was used in this reaction and inspection of the residual solution showed complete 'Brooke rearrangement' of the excess of ketone (**2**) to the silylenol ether (**4**). This rearrangement was also readily catalysed by $[\text{Pd(PPh}_3)_4]$ and [Pt(*trans*-stilbene)$(\text{PPh}_3)_2$]. The published method for this conversion uses mercury(II) iodide[3,4] but this route met with little success in our hands. We find that (**4**) is most readily obtained by addition of 5 mol % $[\text{Pd(PPh}_3)_4]$ to a benzene solution of (**2**) at room temperature, the conversion being almost quantitative.

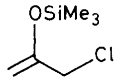
(**1**)

X = Cl, OAc, OS(O)$_2$Me

(**2**)



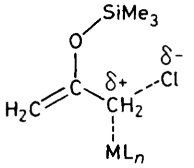
(**3**)



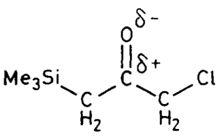
(**4**)

The mechanism for this rearrangement is thought to proceed *via* initial oxidative addition of the C–Cl of (**2**) to the metal centre followed by migration of the Me_3Si group to oxygen and reductive elimination to (**4**). No 'Brooke rearrangement' was observed for the methyl ketone $\text{Me}_3\text{SiCH}_2\text{C(O)Me}$ under analogous conditions suggesting that oxidative addition of the C–Cl bond of (**2**) is an important step in its rearrangement.

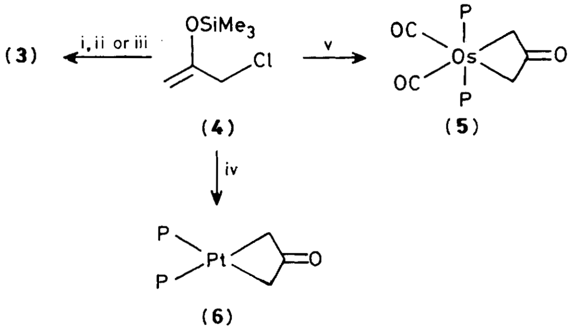
Treatment of the ketone (**2**) with *trans*-$[\text{IrCl(CO)(PPh}_3)_2]$ in refluxing toluene also afforded the metallacyclobutan-3-one (**3**) but whereas this reaction took about 12 h for completion, reaction of the silylenol ether (**4**) with *trans*-$[\text{IrCl(CO)(PPh}_3)_2]$ to give (**3**) was complete within 10 min. We envisage that the silylenol ether (**4**) would be more reactive towards low-valent metal complexes than the ketone (**2**) because the allylic double bond in (**4**) will be more effective at stabilising positive charge at the carbon attached to the leaving chloride in the transition state (A). This stabilisation is not available in the ketone (**2**), representation (B). The reactions of the silylenol ether (**4**) with $[\text{IrH(CO)(PPh}_3)_3]$, [IrH-



(A)



(B)



P = PPh$_3$

Scheme 1. i, $[\text{IrH(CO)P}_3]$; ii, $[\text{IrH(CO)}_2\text{P}_2]$; iii, *trans*-$[\text{IrCl(CO)P}_2]$; iv, [Pt(*trans*-stilbene)P_2]; v, $[\text{Os(CO)}_2\text{P}_3]$.

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† Selected spectroscopic data (coupling constants in Hz). Compound (**3**) i.r. (CsCl disc): $\nu_{\text{C}\equiv\text{O}}$ 2010, $\nu_{\text{C=O}}$ 1635 cm^{-1}; n.m.r. (CDCl_3): ^{1}H (300 MHz) δ 2.47 [m, 2H, (CH_2COCH_2), *J*(HH) 7.9], 2.62 [t, 2H, (CH_2COCH_2), *J*(HH) 7.9], and 7.2—7.7 (m, 30H, PPh_3); ^{13}C{^{1}H} (75.5 MHz) δ 37.1 [s, (*C*H$_2$CO*C*H$_2$)], 164.4 [t, (Ir*C*O), *J*(CP) 4.0], and 197.2 [s, (CH$_2$*C*OCH$_2$)]. Compound (**5**) i.r. (CsCl disc): $\nu_{\text{C}\equiv\text{O}}$ 1995, 1930, $\nu_{\text{C=O}}$ 1610 cm^{-1}; n.m.r. (CDCl_3): ^{1}H (300 MHz), δ 1.5 [t, 4H, (CH_2COCH_2), *J*(HP) 8.22], and 7.3—7.6 (m, 30H, PPh_3); ^{13}C{^{1}H} (75 MHz) δ 27.03 [t, (*C*H$_2$CO*C*H$_2$), *J*(CP) 4.1], 184.1 [t, (Os*C*O), *J*(CP) 10.0], and 191.3 [s, (CH$_2$*C*OCH$_2$)]. Compound (**6**) i.r. (CsCl disc): $\nu_{\text{C=O}}$ 1535 cm^{-1}, n.m.r. (CD_2Cl_2): ^{1}H δ 2.65 [m, 4H, (CH_2COCH_2), *J*(HPt) 45.6], 7.0—7.7 (m, 30H, PPh_3); ^{13}C{^{1}H} δ 49.9 [d, AXX′ system (*C*H$_2$CO*C*H$_2$), *J*(CP) 54, *J*(CPt) 242], ^{31}P{^{1}H} (24 MHz), δ 22.4 [s, *J*(PtP) 3085] p.p.m. (relative to 85% H_3PO_4).

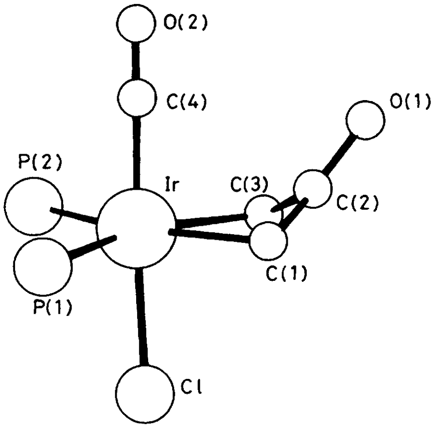
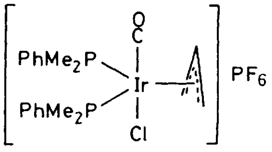


Figure 1. Molecular structure of (**3**) with phenyl rings and H atoms omitted. Interatomic distances: Ir–P(1) 2.432(2), Ir–P(2) 2.432(2), Ir–Cl 2.407(3), Ir–C(4) 1.896(9), C(4)–O(2) 1.05(1), Ir–C(1) 2.169(9), Ir–C(2) 2.561(9), Ir–C(3) 2.184(9), C(1)–C(2) 1.48(2), C(2)–C(3) 1.50(1), C(2)–O(1) 1.21(2) Å. Angles: C(1)–Ir–C(3) 66.5(3), Ir–C(1)–C(2) 87.1(6), C(1)–C(2)–C(3) 106.6(8), Ir–C(3)–C(2) 86.0(5), P(1)–Ir–P(2) 109.9(1)°.

$(CO)_2(PPh_3)_2]$, $[Os(CO)_2(PPh_3)_3]$, and [Pt(*trans*-stilbene)$(PPh_3)_2]$ also gave high yields of a variety of metallacyclobutane-3-ones, Scheme 1.

In previous studies on metallacyclobutan-3-ones of palladium(II) and platinum(II) we have established the presence of highly puckered metallacyclic rings possessing transannular M · · · CO interactions.[5–7] The availability of the iridacyclobutan-3-one (**3**) afforded the opportunity to investigate the structure of this ring system in an octahedral environment and accordingly a single crystal *X*-ray structure determination of (**3**) was carried out.‡

The principal feature of interest in the structure of (**3**) concerns the geometry of the iridacyclobutan-3-one ring (Figure 1). The ring is folded about the line C(1)–C(3) by 41° towards the axial iridium–carbonyl bond. Although this angle is not as large as those found in four-co-ordinate metallacyclobutan-3-ones of platinum(II) and palladium(II) which are in the range 48—53°, it is still substantially more than the 0—10° range found in substituted organic cyclobutanones. This suggests that the alternative formulation of (**3**) as a slipped oxodimethylenemethane complex is still valid. The similar geometry of the iridium allyl (**7**)[8] is relevant to this argument. In (**3**), the tipping of the ring carbonyl towards the Ir carbonyl rather than the chloride ligand is presumably favoured on steric grounds. No ^3J(PC) coupling to the ring carbonyl can be resolved in the $^{13}C\{^1H\}$ n.m.r. spectrum of (**3**),† but it is likely to be smaller than in the platinum compounds[5,7] in view of the weaker Ir–C(2) interaction evidenced by the crystal structure of (**3**).



(**7**)

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‡ *Crystal data* for (**3**): $C_{40}H_{34}ClIrO_2P_2$, $M = 836.3$, triclinic, space group $A\bar{1}$, $a = 18.63(2)$, $b = 18.90(3)$, $c = 10.05(2)$ Å, $\alpha = 99.1(1)$, $\beta = 95.0(1)$, $\gamma = 88.5(1)°$, $Z = 4$, $D_c = 1.596$ g cm^{-3}, Mo-K_α *X*-radiation, $\bar{\lambda} = 0.71069$ Å, μ(Mo-K_α) = 38.6 cm^{-1}; final $R = 0.054$ (R_w 0.058) for 5963 independent reflections [$I \geqslant 2.5\sigma(I)$] collected at 293 K on a Stoe STADI-2 Weissenberg diffractometer in the range $7 < 2\theta < 54°$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

1 M. D. Jones, R. D. W. Kemmitt, A. W. G. Platt, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Chem. Commun.*, 1984, 673.
2 M. D. Jones and R. D. W. Kemmitt, *J. Chem. Soc., Chem. Commun.*, 1985, 811.
3 H. Sakurai, A. Shirahata, Y. Araki, and A. Hosomi, *Tetrahedron Lett.*, 1980, **21**, 2325.
4 O. V. Litvinova, Yu I. Baukova, and I. F. Lutsenko, *Dokl. Akad. Nauk. SSSR*, 1967, **173**, 279.
5 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, P. McKenna, D. R. Russell, M. D. Schilling, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1984, 1993.
6 R. D. W. Kemmitt, P. McKenna, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1985, 259.
7 A. Imran, R. D. W. Kemmitt, A. J. W. Markwick, P. McKenna, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1985, 549.
8 J. A. Kaduk, A. T. Poulos, and J. A. Ibers, *J. Organomet. Chem.*, 1977, **127**, 245.

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